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Synopsis

In the present experiment, the conditions and the mechanisms of electrolytic polishing with respect to various copper alloys of the Cu-Zn, Cu-Al and Cu-Al-Zn system have been investigated by obtaining the Jacquet's characteristic curves, and Jacquet's curves have been also measured for the effects of additional elements on these alloys. In these experiments, it has been found that the effect of aluminium is greater than that of zinc; and that the surface of alloys showing two or three phases cannot be well polished under the present experimental condition, and that the glossy surface which appears after the electrolytic polishing is due to the occurrence of cuprous oxides.

I. Introduction

The electrolytic polishing method, well known since the investigation of Jacquet, has been applied to several metals. Previous studies were directed chiefly to the pure metals and for the alloys, only stainless steel and brass were the object of investigation because of their most popular use. But so far as we know, the method has scarcely been systematically studied, so that it often failed for the application to alloys. We have undertaken the present investigation on the system of Cu-Zn, Cu-Al and Cu-Al-Zn alloys in order to learn the conditions and the mechanisms of electrolytic polishing of alloys qualitatively, by measuring the voltage-current density curve.

II. Apparatus and Method of Experiment

For experiment we used almost the same apparatus and method as generally employed in studies on electrolytic polishing of copper series alloys (Fig. 1).

Ethyl alcohol was added as the inhibiter for better polishing and ortho-phosphoric acid was used in order to reduce the loss of liquid, when a sample is taken from the liquid.

Since the voltage-current density curve varies according to the measuring methods of voltage, we took enough care that the measurement was made under the equilibrium state, changing the voltage by 0.1 valt.

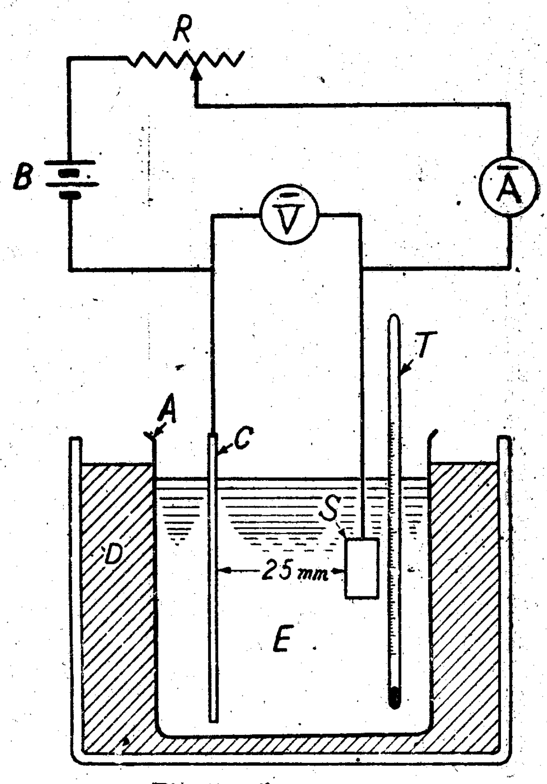

Fig. 1. Apparatus

A : Electrolytic bat.
B : Electric source ; battery 4 V.
C : Cathode ; electrolytic copper 1 mm rolled plate (68×85 mm).
D : Constant temperature bath.
E : Electrolyte: ortho phosphoric acid (d-1.44) and 3% ethyl alcohol.
R : Slide resistance.
S : Sample.
T : Thermometer.

Samples: The metals, mixed in the required weight proportion, were melted by 7 K. V. A. Ajax type high frequency furnace in Tammann's porcelain tubes, and the molten alloys were cast in a 10 mm diameter chill-mould, cut 5 mm in thickness, annealed for an hour at 800℃ and then cooled in the furnace. The surface of each sample was polished with emery paper and the other faces were sealed by paraffin.

The number, composition and phase of samples are as shown in Tab. 1.

Table 1 Composition of Samples

No.	Composition			Phase
	Cu	Zn	Al	
0	100	0	0	α
1	95	5	0	α
2	90	10	0	α
3	85	15	0	α
4	80	20	0	α
5	75	25	0	α
6	70	30	0	α
7	65	35	0	$\alpha+\beta$
8	60	40	0	$\alpha+\beta$
9	55	45	0	β
10	50	50	0	β
11	99	0	1	α
12	98	0	2	α
13	97.5	0	2.5	α
14	97	0	3	α
15	96	0	4	α
16	95	0	5	α
17	94	0	6	α
18	90	0	10	$\alpha+\gamma$
21	94	5	1	α
22	89	10	1	α
23	84	15	1	α
24	79	20	1	α
25	74	25	1	α
26	69	30	1	$\alpha+\beta$
27	64	35	1	$\alpha+\beta$
28	59	40	1	$\alpha+\beta$
29	54	45	1	β
30	49	50	1	$\beta+\gamma$
31	92.5	5	2.5	α
32	87.5	10	2.5	α
33	82.5	15	2.5	α
34	77.5	20	2.5	α
35	72.5	25	2.5	$\alpha+\beta$
36	67.5	30	2.5	$\alpha+\beta$
37	62.5	35	2.5	$\alpha+\beta$
38	57.5	40	2.5	β
39	52.5	45	2.5	$\beta+\gamma$
41	91	5	4	α
42	86	10	4	α
43	81	15	4	α
44	76	20	4	α
45	71	25	4	$\alpha+\beta$
46	66	30	4	$\alpha+\beta+\gamma$
47	61	35	4	β
48	56	40	4	$\beta+\gamma$

III. Experimental Results

1. The system of Copper and Zinc.

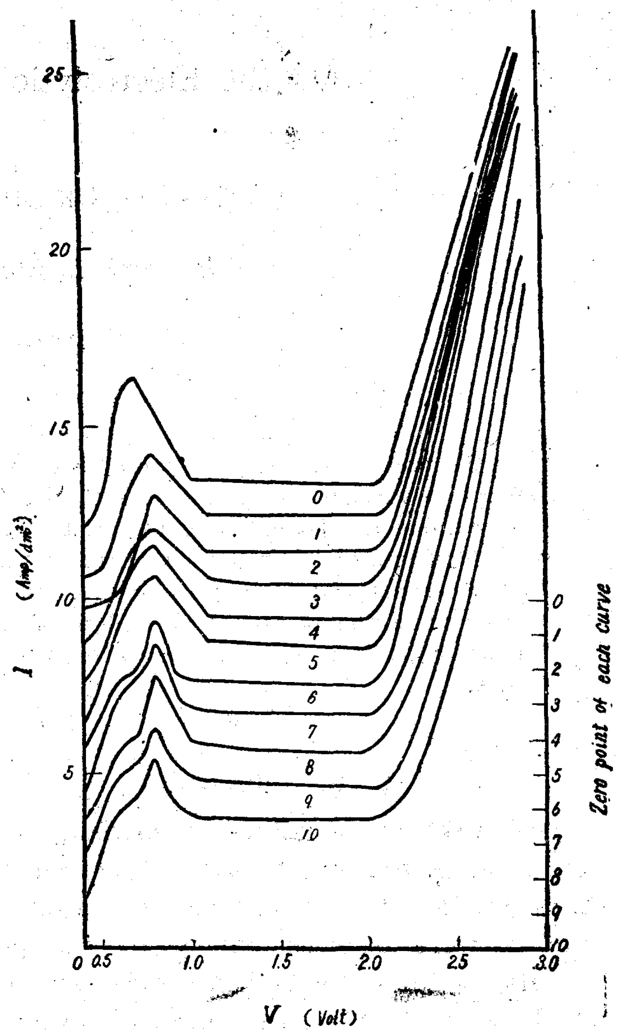

Fig. 2. I-V curves of Cu-Zn system alloys.

The photograms of voltage-current density of this system are given in Fig. 2. In the case of pure copper, there were points in some range of voltage, in which it was unable to obtain a current in equilibrium owing to sudden changes. These range were diminished according to the increase of zinc.

A characteristic curve was obtained almost continuously for more than 30% zinc, and there was found a kink point at the ascending part of the curve near 0.7 volt, probably due to the effect of zinc.

Any apparent difference of electric current density due to the zinc percentage was not observed in this experiment. In the range of the experiments, it has been demonstrated that by the electrolytic polishing of one phase, quite smoothly polished surface could be obtained but not by that of two phases.

2. The system of Copper and Aluminium.

As shown in Fig. 3, we obtained a characteristic curve in which the minimum point was appeared near 0.8 volt by the addition

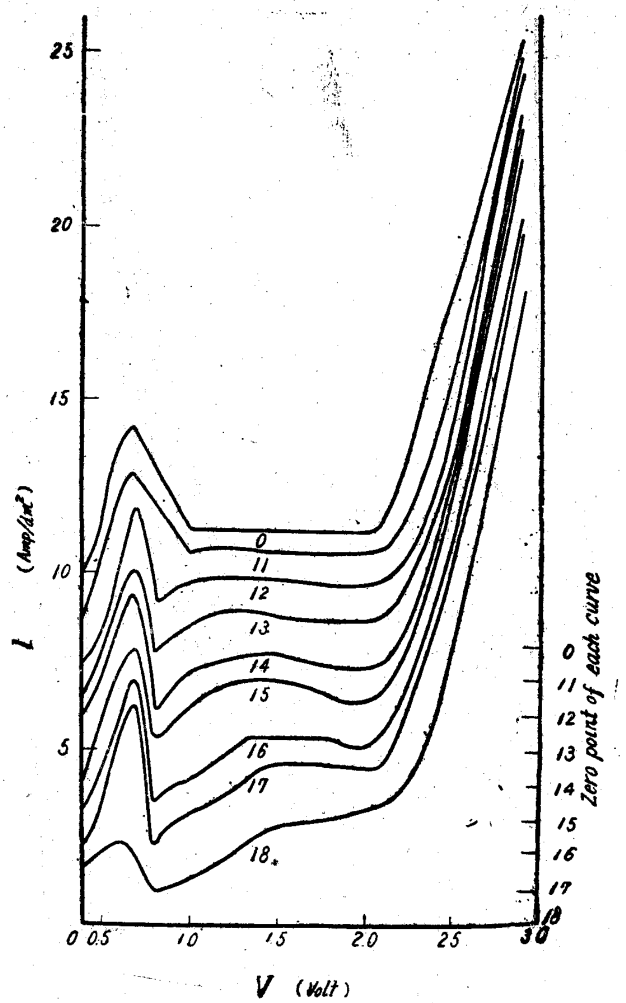

Fig. 3. I-V curves of Cu-Al system alloys.

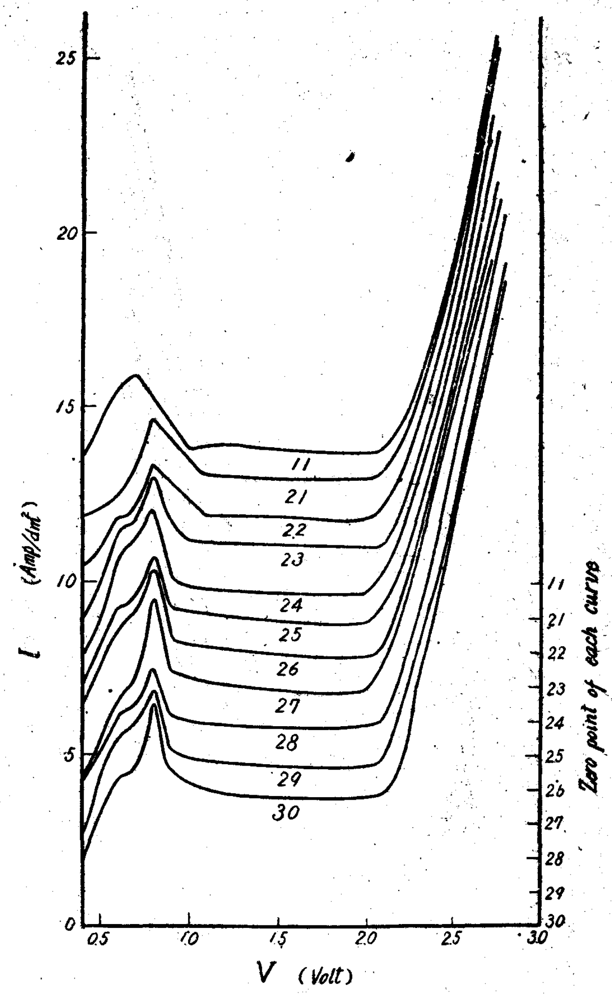

Fig. 4. I-V curves of Cu-Al-Zn system alloys (Al 1%).

of more than 2% aluminium and the increase of aluminium percentage resulted in the lowering of the minimum point in the curve. Although the horizontal part of curve was not so clear in comparison with the case of the Cu-Zn system, it was noticed that an increase of aluminium resulted in enlarging the convex part of the curve. More than 5% aluminium caused the convex part gradually to disappear and consequently the length of the horizontal part of curve became very short. In the case of 10% Al, the first maximum of the curve fell down and the minimum and next bending part were gradually diminished. Then, the form of the curve became flat. The minimum point of the curve is probably due to the effect of aluminium. In this experiment we were able to obtain a glossy surface in only one phase.

3. The system of Copper Aluminium and Zinc.

a) 1% Aluminium. (Fig. 4)

In this case, the addition of aluminium showed no remarkable change in the characteristie curve. However, from the occurrence of the kink point of the first ascending curve, it was suggested that both the addition of aluminium and the increase of zinc have the same effect on the curve. The kink point of the curve appeared from 10% zinc and the appearance on the horizontal part of the curve resembled to the Cu-Zn system.

b) 2.5% Aluminium. (Fig. 5)

When aluminium is added constantly in the ratio of 2.5%, there are seen two maxima in the curve, as in the Cu-Al system. The effect of aluminium was so distinct; a horizontal part continued to the minimum and moreover, a convex part followed them. The deepness of the minimum and the degree of bending in the convex part, decreased with the increase of zinc in the sample. The kink point in the first ascending part in the Cu-Zn system, appears from 5% zinc. With the increased zinc percentage the kink point becomes more remarkable, and the curvature

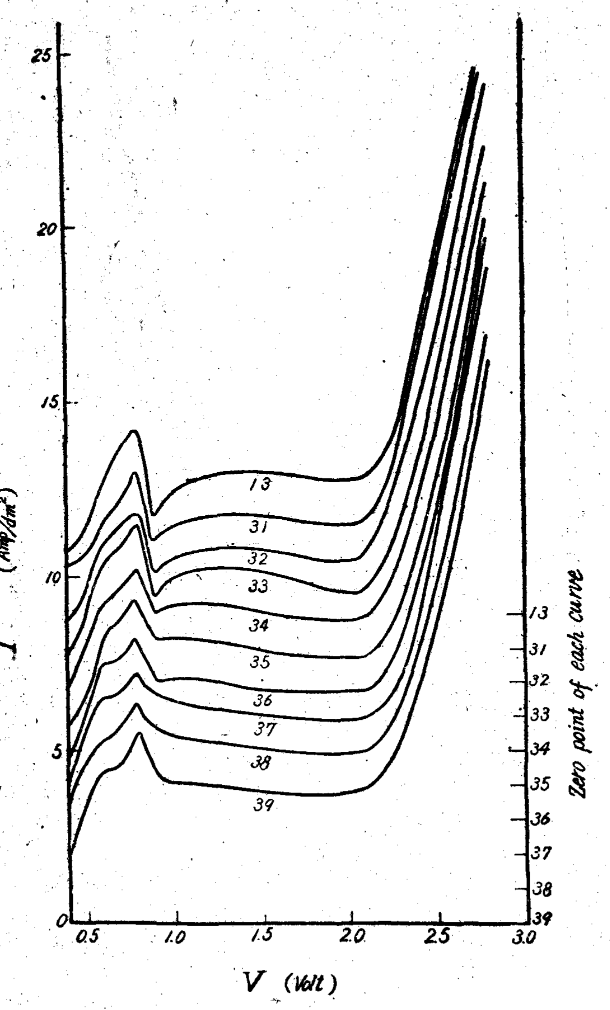

Fig. 5. I-V curves of Cu-Al-Zn system alloys (Al 2.5%).

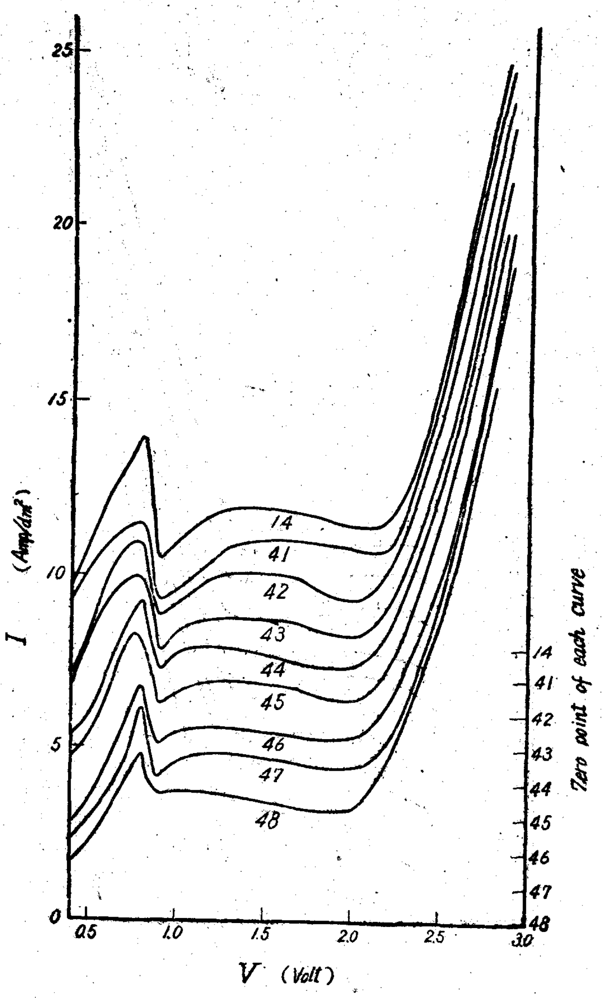

Fig. 6. I-V curves of Cu-Al-Zn system alloys (Al 4%).

at the convex part of the curve was lessened, approaching to horizantal.

c) 4.0% Aluminium. (Fig. 6)

If the zinc percentage is increased from 5% to 40%, while aluminium percentage is fixed in 4%, the effect of aluminium is found to exceed that of zinc, that is to say, the kink point of the first ascending part, which is thought to be the effect of zinc, is not presented. Then, the minimum, which continues the maximum, and the convex part appear distinctly. With the increase of zinc there is seen a tendency that the minimum of the electric current density becomes gradually higher.

The minimum point of the curve can be observed from the samples of higher Zn content, in comparison with the cases of 1% or 2.5% Al. Just for the sample of 40% Zn, this minimum point disappears but the convex part doesn't vanish yet.

IV. Discussion

1. The system of Copper and Zinc.

In the alloys of Cu-Zn system the voltage-current density curve of electrolytic polishing presents the shape of Jacquet's curve.[1] Increasing the voltage, anode dissolves into electrolyte and when it reaches a certain strength, there is produced a passive state at the surface of the metal so that the current is suddenly lowered, thus the maximum point of the curve is formed. Further increase of the voltage gives no change of the current and the polishing can be accompolished at this part of the curve.

When the voltage reaches a certain height, the passive state is broken and the current increases suddenly with the outbreak of oxygen.

The fact that the type of the characteristic curve of Cu-Zn system alloys is not so different from the curve of copper, suggests that the passive state which appears in this system resembles that in copper. It has been already ascertained that on the electrolytic-polished surface there was formed cuprous oxide in both cases of copper[2] and brass.[3][4] The difference of the curve owing to the phase change couldn't be recognized for the alloys of Cu-Zn system. It may be due to the reason that ths characteristic curve shows the behaviour of the passive state. From this point of view, it may be said contrariwise that the addition of zine is followed by the formation of kink point before the first maximum of the curve. And it seems that the passive state of zinc is produced on the surface selectively, but broken soon, for it is very weak, and then the passive state of copper appears, which can be found as the polished surface on the metal. The reverse electro-motive force between the passive state and the ground metal is so large that there are some points on the curve, at which the current cannot be measured, but it is reduced with the increased zinc percentage.

When there is the mixture phase of α and β, we can obtain only a rough, not perfectly polished surface, for each velocity of solubility is different. Then β phase can be polished as well as α phase, and when γ compound appears, $\beta+\gamma$ mixture does not present a glossy surface. We must find other conditions in order to obtain a flatter polishing surface from the sample of two phases.

The system of Copper and Alumnium.

When we take the alloys of Cu-Al system in consideration on similar way as was above mentioned, we can find the characteristics of the curve more distinctly. It is observed that with the addition of aluminium, the characteristic curve is changed remarkably from the copper curve. Addition of only 1%, the effect of Al can be recognized already, that is to say, there appears the miminum point before the horizontal part which follows the maximum of the curve.

By increasing the percentage of aluminium there comes out the bowed bending part. This minimum is due to the film of aluminium in the passive state, which should be produced by the selective oxidation of aluminium in the Cu-Al system alloy. And it agrees to some extend with the result of study,[5] that by the addition of more than 2% Al the oxidation at high temperature can be prevented. According to the increased alumnium percentage, the resistance of the passive state of aluminium becomes higher. And the minimum point of the curve becomes deeper. If the aluminium passive state is broken by increasing the voltage, then is produced the copper passive state on the surface of the metal. Horizontal part of the curve, which is thought to be the characteristic of copper, becomes shorter and at last disappears at 10% aluminium. In this case the voltage, in which the oxide on the surface disappears seems to be slightly higher than in the case of copper.

The last state of the surface seems to be cuprous oxide as in the Cu-Zn system, if there is a horizontal part in the curve; on the other hand, if there is no horizontal part, it may be aluminium oxide.

3. The system of Copper, Aluminium and Zinc.

The same experiments were made on the ternary alloys of Cu-Al-Zn system. In the case of 1% Al alloys the characteristic curve was nearly equal to the curve of the Cu-Zn system. The addition of aluminium corresponds to the increase of zinc; when aluminium is added, the effect of zinc is accelerated, so that low percentage of Zn produces the zinc passive state. We consider that by this aluminium percentage, the aluminium passive state does not appear remarkably. In the case of 2.5% aluminium influence of aluminium is quite remarkable. With the increase of zinc percentage as in other cases, the minimum point of the curve decreases gradually, but the effect of Al can hardly be seen when the zinc percentage becomes higher.

In the 4% aluminium series, the influence of aluminium exceeds that of zinc, that minimum point of the characteristic curve does not disappear for the samples of high zinc percentage, In the case of ternary alloy like that of Cu-Zn, and Cu-Al alloys, the selective oxidation is different according to the amount of element added but it is confirmed that the influence of aluminium is remarkable compared with zinc.

In the range of this expesiment, it is suggested that electrolytic polishing can be done well in one phase but not in two or three phases under the same condition. Judging from the characteristic curve, it seems that in the case of ternary system like that of Cu-Zn system, the polished surface is of cuprous oxide. Fortunately, we could obtain a golden coloured surface equal to gold by means of electrolytic polishing of this ternary alloys. This colour is different from that of the ground, and is thought to be due to oxidized film or that produced by the interference between oxidized film and ground metal.

Wa think that the studies upon the nature of the oxides which is produced on the surface by electropolishing should be performed by the method of electron diffraction.

Summary

The experimental results obtained from the Jacquet's characteristic curve of Cu-Zn system Cu-Al system and Cu-Al-Zn system are as follows:

(1). In the case of copper and zinc system, there appears a kink point on the ascending curve by adding more than 30% zinc. However, the curve itself is nearly equal to copper's characteristic curve.

(2). In the case of copper and aluminium system, there is found a great difference from the copper case; this is well indicated by the minimum and the next bowed bending part in the characteristic curve.

(3). In the case of copper, aluminium and zinc system, the effect of aluminium is stronger than that of zinc.

(4). In one phase each element of alloy is selectively oxidized according to the percentage of composition, but after all the one which gives the glossy surface by electrolytic polishing is perhaps the copper passive state.

(5). In the case of two or three phases it connot be well polished under the present experimental conditions.

(6). In spite of quite different solving velocity among phases, we cannot recongnize remarkable difference in the characteristic curve in the range of the present experiment.

It may be by the reason that the curve depends upon the behavior of the passive film on the metal surface.

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